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FINAL REPORT FOR ONR CONTRACT N00014-95-1-0122

Title: SELECTED ENERGY EPITAXIAL DEPOSITION (SEED) AND LOW ENERGY ELECTRON MICROSCOPY (LEEM) OF AlN, GaN and SiC THIN FILMS

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Long term goals:

- Epitaxial growth of wide band gap Group III-nitride semiconductors using seeded-beam supersonic jet sources (SSJ) and selected energy epitaxy (SEED).

- Determination of the kinetics and mechanisms of homoepitaxial and heteroepitaxial growth of the aforementioned III-Nitride thin films using low energy electron microscopy (LEEM).

Objectives:

- Optimize low-temperature growth of GaN using seeded supersonic molecular beams of NH_3 and triethylgallium (TEG).

- Determine the optimum growth parameters by conducting *in situ* real-time observations of the heteroepitaxial growth of GaN(0001) on 6H-SiC(0001) substrates using the SSJ source seeded with NH_3 with the low-energy electron microscope (LEEM).

- Investigate effects of precursor translational energy on growth kinetics and morphology of GaN films.

Approach:

North Carolina State University (NCSU)

- Seeded supersonic molecular beams were employed to supply translational energy to surmount activation barriers to precursor decomposition and enhance adatom mobility in GaN epitaxial growth [1].

Arizona State University (ASU)

- An ammonia flux was supplied from the seeded beam SSJ source connected to the LEEM, as shown in the schematic diagram Fig. 1. The Ga flux was supplied from an evaporative cell. The substrate was a 6H-SiC(0001) wafer cleaned by a high-temperature etching treatment at 1600°C in atmospheric hydrogen to remove surface scratches and to reveal atomic steps prior to mounting in the LEEM. The substrate temperature and the ratio of the flux species can be independently adjusted during growth under LEEM observation.

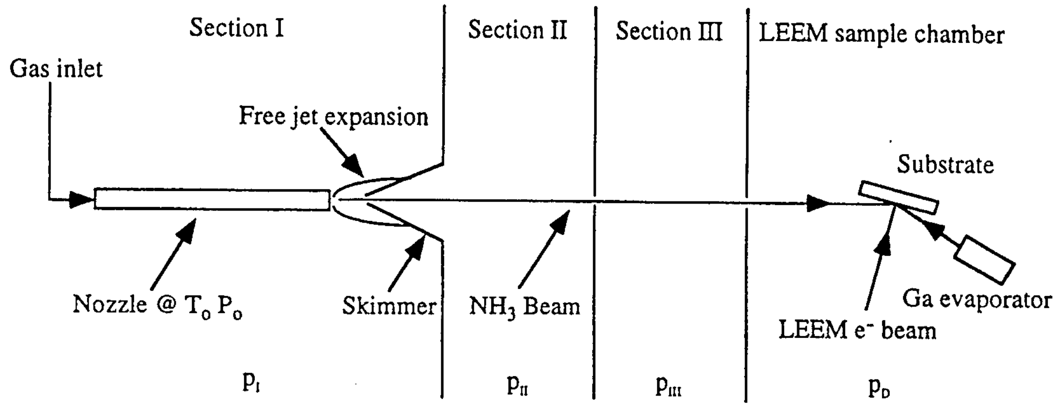

Figure 1. Schematic diagram of the SSJ source connected to the LEEM sample chamber for GaN growth at ASU. Pressures during deposition: $P_o = 1000$ Torr; $P_I = 5\times10^{-4}$ Torr; $P_{II} = 1\times10^{-6}$ Torr; $P_{III} = 1\times10^{-7}$ Torr; and $P_D = 3\times10^{-8}$ Torr.

Work Completed:

North Carolina State University

- Gas-source molecular beam epitaxy (GSMBE) of GaN on high-temperature MOVPE GaN/AlN/SiC substrates using an effusive Ga source and NH_3 from an ultra-high vacuum (UHV) leak valve.

- Homoepitaxial growth of GaN using seeded supersonic molecular beams of NH_3 and an effusive Ga source.

- Homoepitaxial growth of GaN using seeded supersonic molecular beams of TEGa and NH_3 from a UHV leak valve.

Arizona State University

- Heteroepitaxial growth of GaN directly on 6H-SiC(0001) substrates was observed in the LEEM at growth temperatures in the 600-700°C range. The flux ratio of Ga/NH_3 was adjusted during each growth to achieve two-dimensional (2D) basal-plane oriented layers without facets.

Results:

North Carolina State University

- Measurement of Ga and NH_3 incorporation efficiencies in gas source molecular beam epitaxy (GSMBE) of GaN under Ga-limited and N-limited conditions, respectively.

- Correlation of the surface roughness of GSMBE GaN films with V/III ratio and growth rate. Observed e vidence of statistical roughening (quenched growth) for films grown under NH_3-rich conditions.

- Systematic investigation of the effect of NH_3 translational energy on GaN growth rate using carrier gases with different molecular weights (He, H_2, N_2, and Ar) and a wide range of nozzle temperatures. Energy barrier for NH_3 dissociative chemisorption was found to be negligibly small (less than 0.05 eV), contrary to a preliminary report by Torres and coworkers [2]. The data are consistent with a precursor-mediated mechanism for NH_3 dissociative chemisorption. Vibrational excitation of the incident NH_3 molecule apparently increases the rate of barrier crossing between the precursor state and the dissociatively chemisorbed state.

- The focusing effect of light carrier gases (He and H_2) produces intense NH_3 beams (fluxes > 4×10^{14} $cm^{-2}s^{-1}$ at the substrate) for low NH_3 seeding percentages (< 5 vol.%). Rough, highly faceted, surface morphologies were observed for films grown under Ga-limited (NH_3-rich) conditions.

- Very smooth, homoepitaxial GaN films (1.2 nm RMS roughness) were grown using seeded supersonic beams of TEGa and NH_3 from a UHV leak valve. The growth rate was approximately 60 nm/h at 750°C. The growth rate depends on the TEGa and NH_3 fluxes, in contrast to GSMBE, where the flux of one precursor is typically rate-limiting.

Arizona State University

The Ga/NH_3 flux ratios employed to achieve growth of two-dimensional GaN layers were strongly dependent on the growth temperature. At lower growth temperatures, i.e. around 600°C, an NH_3-rich flux ratio was required; while at higher temperatures, i.e. near 700°C, a Ga-rich flux ratio was preferable.

A typical growth sequence starts with the clean 6H-SiC(0001) substrate surface as shown in Fig. 2. Time-lapsed LEEM images frame captured during growth at 600°C are shown in Fig. 3. The Ga flux was 0.89×10^{13} cm^{-2} s^{-1} and the NH_3 flux was 3.30×10^{13} cm^{-2} s^{-1} giving a Ga/NH_3 ratio of 0.27. It can be observed in frame (b) of Fig. 3 that after 17 min of deposition, the steps of the SiC substrate were obscured. They reappeared again in frame (d), after 25 min of deposition. The surface appeared unchanged after about 1 hour, retaining a grainy appearance with the steps visible as shown in frames (e) and (f).

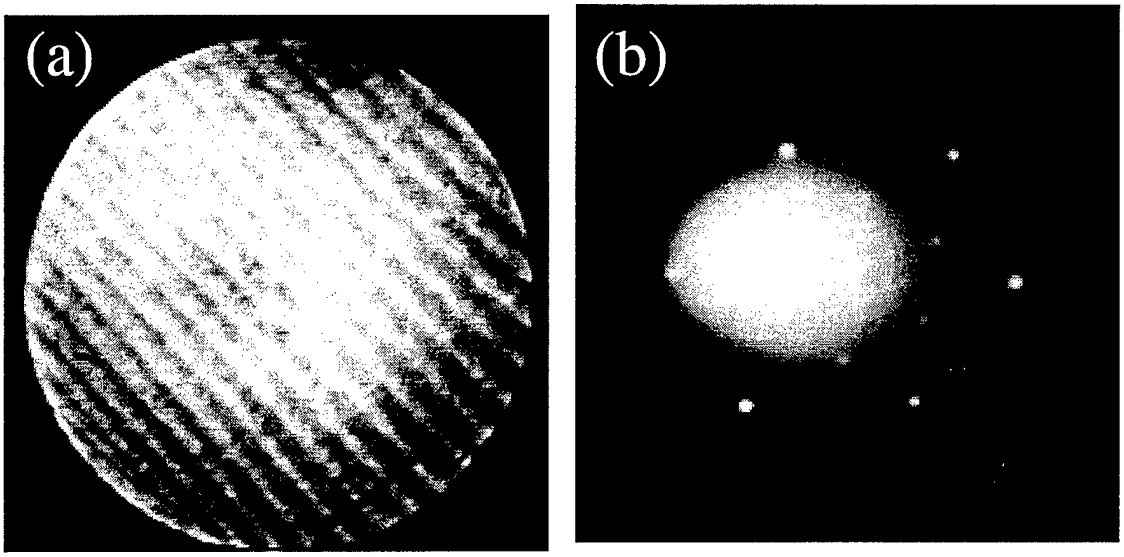

Figure 2. (a) LEEM image of a clean 6H-SiC(0001) substrate surface showing terraces and steps. Field of view is 4.8 microns. (b) the $\sqrt{3} \times \sqrt{3}$ LEED pattern of the SiC substrate surface.

The GaN layer after 3 hours of growth was flat and non-faceted; its surface morphology is shown in the AFM images in Fig. 4. The layer shows a (1×1) LEED pattern, indicating basal plane growth. The thickness of this layer was about 10 nm. It appears that the GaN layer was formed from the coalescence of small 2D islands. Indeed, nearly all non-faceted 2D GaN layers grown by the SSJ method have similar morphologies. At higher growth temperatures, e.g., at 655°C and at similar flux rates, a higher Ga/NH_3 ratio, ~ 1.5, was required to achieve such a morphology. An NH_3-rich growth condition at higher growth temperatures would result in a faceted layer. Conversely, a Ga-rich condition at lower growth temperatures would produce Ga droplets and very slow growth rates.

The growth process leading to the formation of the 2D GaN(0001) layers is shown in the AFM images of Fig. 5. Because of the 16° grazing incidence of the flux species determined by the imaging geometry of the LEEM, different areas on the substrate surface exhibit different coverage levels. The AFM images in Fig. 5 taken on different regions of the substrate basically reflect the different growth stages. The growth proceeds via nucleation of flat 2D islands at the step edges of the 6H-SiC(0001) substrate surface as shown in Fig. 5(a). These islands grow laterally at a much a higher rate than their vertical growth rate, increasing in size as shown in Fig. 5(b). This lateral growth mechanism is evident from the fact that almost all the islands straddle both sides of the steps. This particular growth stage leads to the loss of resolution of the steps in the LEEM image of Fig. 3(b). As deposition continues, the islands finally coalesce and form a continuous layer as shown in Fig. 5(c). The coalescence occurs over ~200 nm wide terraces, and the coalesced layer has a thickness of ~20 nm. This gives a lateral to vertical growth ratio of ~10. The growth process revealed by our study is very similar to the model of quasi-2D island growth proposed by Headrick, *et al.* [3] in their x-ray scattering studies of GSMBE growth of GaN. Their growth model is illustrated in Fig. 6. The shape of the 2D GaN islands can be observed in the cross-sectional TEM image of a GaN layer grown on SiC as shown in Fig. 7. These islands bear a remarkable resemblance to those proposed by Headrick, *et al.* [3].

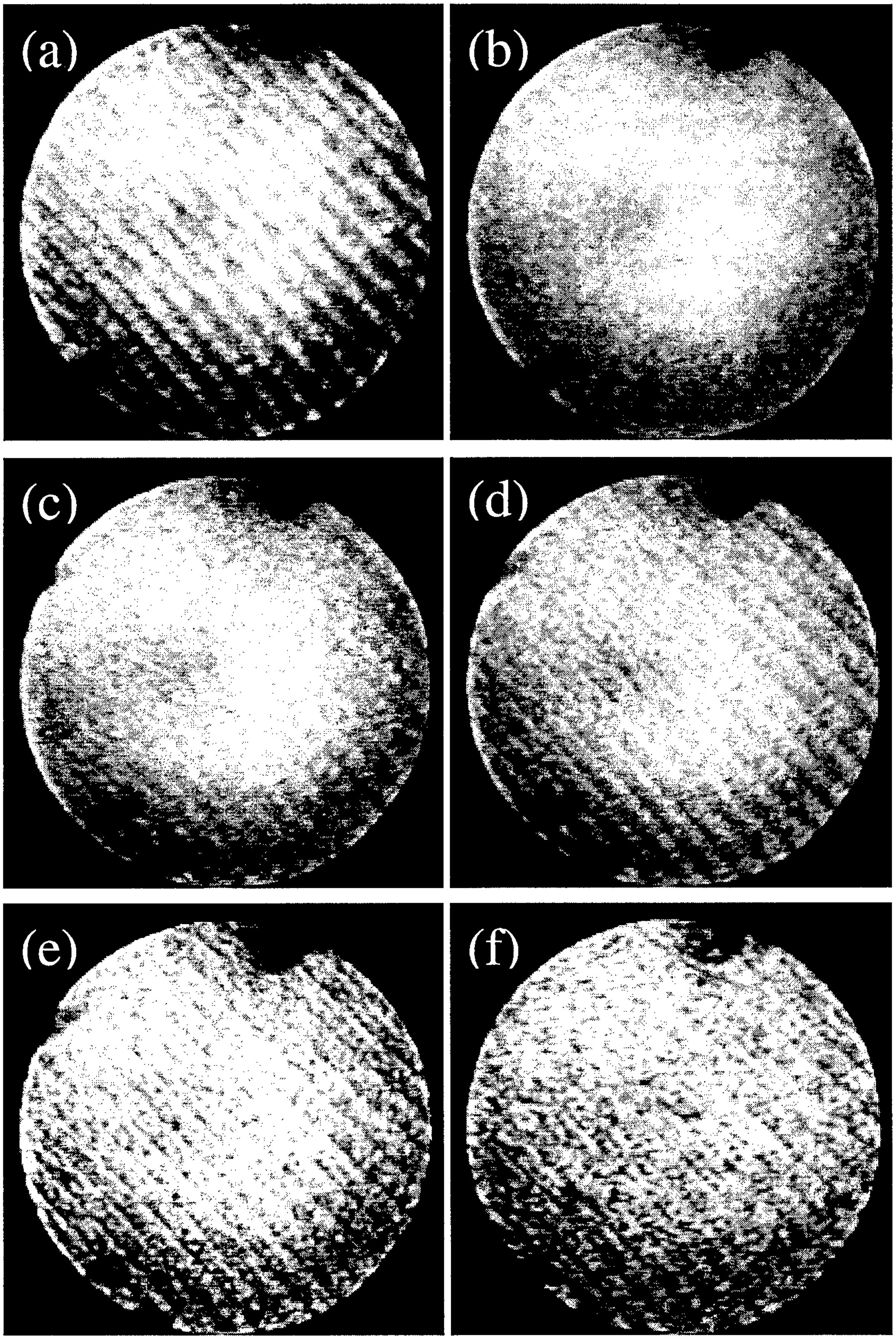

Figure 3. Frame-captured LEEM images of SSJ growth of GaN on 6H-SiC(0001). Field of view is 4.8 μm. The deposition times of the frames are: (a) 13 min, (b) 17 min, (c) 19 min, (d) 25 min, (e) 58 min, and (f) 126 min.

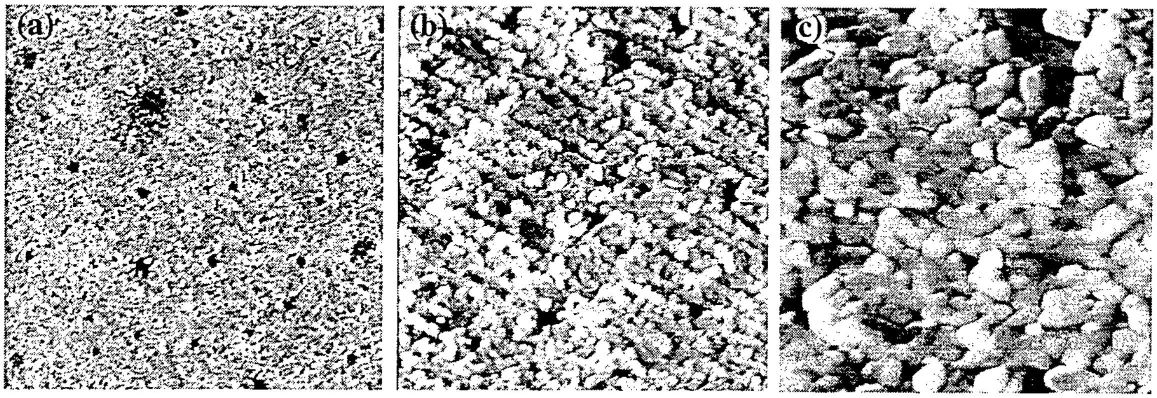

Figure 4. AFM images of the GaN layer in Fig. 3 after 3 h of growth. Scan siz; (a) 10 micron × 10 micron; (b) 5 micron × 5 micron, and (c) 2 micron × 2 micron.

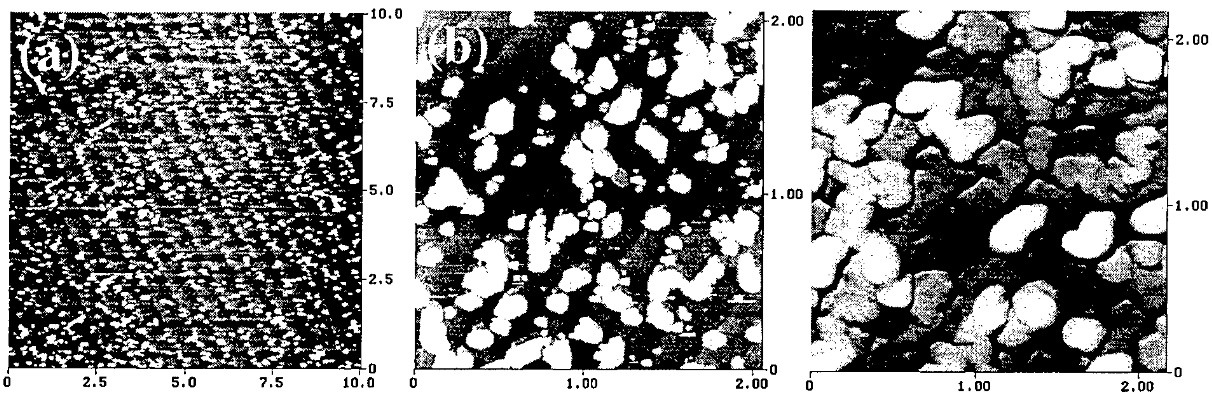

Figure 5. AFM images of the growth on 6H-SiC(0001) at 600°C using the seeded beam SSJ source. The Ga/NH_3 ratio used in this growth was 0.49. Images (a) and (b) show initial nucleation at the step edges of the SiC substrate. Image (c) shows coalescence of the 2D GaN islands into a continuous film. The scale in μm is indicated on each image.

Impact/Applications:

Selected energy epitaxial deposition using seeded supersonic beams of TEG provides an alternative to gas source molecular beam epitaxy (using NH_3 or plasma-generated N) for low-temperature (700-750°C) epitaxial growth of high-quality GaN films. Flat two-dimensional GaN(0001) layers can be grown directly on 6H-SiC(0001) substrates using seeded beam SSJ sources. To achieve this, the Ga/NH_3 flux ratio must be carefully chosen depending on the growth temperature. At low growth temperatures, ~600°C, NH_3-rich conditions are necessary; whereas, at higher growth temperatures, ~700°C, Ga-rich conditions are preferable. Adherence to these growth conditions allows epitaxial GaN(0001) to be grown on 6H-SiC(0001) substrates without the use of an intermediate AlN buffer layer. The elimination of the insulating AlN layer allows the fabrication of vertical structures for electronic devices with top and backside contacts.

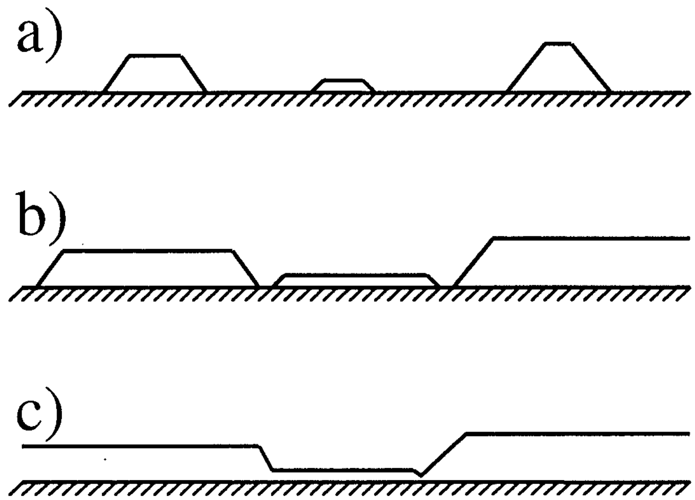

Figure 6. Schematic diagram of the growth and coalescence of the 2D GaN islands; taken from Headrick *et al.* [3].

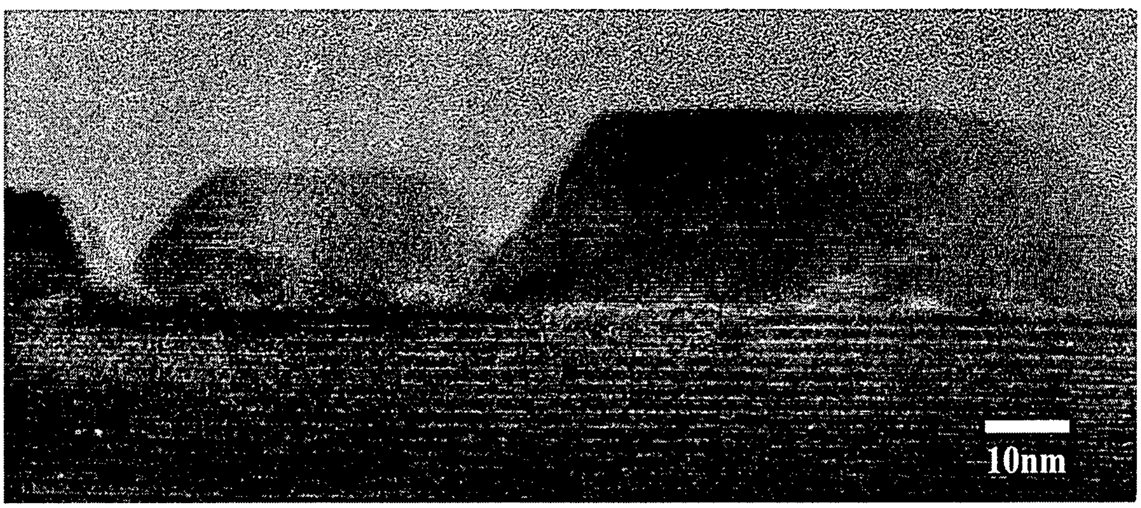

Figure 7. Cross-sectional TEM image of the 2D GaN islands grown on a 6H-SiC(0001) substrate. Most of the GaN islands imaged by TEM show a mixture of hexagonal and cubic layers.

Transitions:

None

Related Projects:

None

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Patents:

1. I.S.T. Tsong, D.J. Smith, V.M. Torres, J.L. Edwards and R.B. Doak. "Method for forming a low-defect epitaxial layer in the fabrication of semiconductor devices". US Patent File No. AP31672-072448.0262, October 9, 1998.